

UNCLASSIFIED

Defense Technical Information Center
Compilation Part Notice

ADP023623

TITLE: Detailed and Simplified Chemical Kinetics of Aviation Fuels and Surrogates

DISTRIBUTION: Approved for public release, distribution unlimited

This paper is part of the following report:

TITLE: Army Research Office and Air Force Office of Scientific Research Contractors' Meeting in Chemical Propulsion Held in Arlington, Virginia on June 12-14, 2006

To order the complete compilation report, use: ADA474195

The component part is provided here to allow users access to individually authored sections of proceedings, annals, symposia, etc. However, the component should be considered within the context of the overall compilation report and not as a stand-alone technical report.

The following component part numbers comprise the compilation report:
ADP023616 thru ADP023650

UNCLASSIFIED

DETAILED AND SIMPLIFIED CHEMICAL KINETICS OF AVIATION FUELS AND SURROGATES

Grant Number FA8655-06-1-3052

R.P. Lindstedt

Department of Mechanical Engineering, Imperial College London,
Exhibition Road, London SW7 2 AZ, UK.

SUMMARY/OVERVIEW

The removal of the high Damköhler number assumption from modeling approaches is essential for the computational simulation of combustor flows where strong direct kinetic effects are present. Examples of relevant physical phenomena include flame extinction and re-light as well as pollutant emissions. Calculation methods (e.g. LES/FMDF) aimed at including such effects are computationally demanding and simplified reaction mechanisms that represent the desired chemical features with sufficient accuracy are required. Difficulties are augmented for aviation fuels due to the wide range of fuel components and sufficiently accurate detailed surrogate mechanisms are required for the subsequent derivation of further simplifications under actual operating conditions prior to the implementation into calculation methods for turbulent flows. The present paper addresses the issue of substituted aromatics and outlines a reaction class based route to the derivation of detailed chemical kinetic mechanisms. The example given considers the toluene/1-methyl naphthalene system.

TECHNICAL DISCUSSION

Flow timescales encountered in high performance propulsion devices increasingly lead to difficulties associated with kinetically controlled or influenced phenomena such as flame stability, extinction and re-light [1]. The accuracy of surrogate fuel models ultimately needs to be assessed with respect to the reproduction of selected key parameters in practical applications. The issue is therefore arguably best addressed in the context of turbulent flame simulations where the relative impact of flow and chemistry can be assessed. However, operating conditions of practical devices are typically far removed from the conditions under which validation of computational sub-models is possible. In the present context, detailed chemical kinetic models are then required to (i) facilitate the extrapolation to relevant conditions and (ii) serve as a basis for further simplifications under such conditions. The current paper illustrates the use of a reaction class based approach for the generation of detailed chemical mechanisms for substituted aromatics such as 1-methyl naphthalene. The subject is challenging and the use of chemical similarities with the oxidation of cyclopentadiene, benzene and toluene is explored in the context of quantitative species predictions.

The starting point for the toluene sub-mechanism stems from Lindstedt and Maurice [2] with subsequent developments by Potter [3] and as part of ongoing work. The mechanism consists of 88 reactions and 13 species and considers oxidation and pyrolysis of the CH₃ group as well

as radical attack on the ring. The underlying small hydrocarbon chemistry exerts a significant influence and was derived using a hierarchical approach [2,3]. An analysis of uncertainties and a reconciliation of sub-mechanisms with those produced by other workers forms part of the current effort. The corresponding mechanism for 1-methyl naphthalene oxidation was based directly on the equivalent toluene reactions and features decomposition and radical attack on the aromatic rings and the methyl group. The mechanism has also been applied to model the oxidation of species such as naphthalene with encouraging results [3].

A wide range of conditions has been used to validate the toluene sub-mechanism. However, the scarcity of experimental data for higher substituted aromatics presents a significant limitation in the context of validation of proposed reaction mechanisms. In the present case, the obtained accuracy is illustrated by comparisons with experimental data for toluene and 1-methyl naphthalene obtained in a Jet Stirred Reactor (JSR) [4,5]. The single case presented here was chosen to facilitate direct comparisons of toluene and 1-methyl naphthalene oxidation under similar conditions. The toluene data was obtained at a stoichiometry (ϕ) of 1.5, $1000 < T \text{ (K)} < 1380 \text{ K}$, a mean residence time (τ) of 120 ms and at atmospheric pressure. The dominant fuel consumption paths at higher temperatures under these conditions is via $\text{C}_7\text{H}_8 + \text{H/OH} = \text{C}_7\text{H}_7 + \text{H}_2/\text{H}_2\text{O}$ (1). The adopted rates follow the CEC recommendations by Baulch et al. [6]. The consumption of toluene and oxygen is reproduced with reasonable accuracy along with the formation of primary aromatic products such as benzene, styrene and ethyl-benzene as shown in Fig. 1. The generation of H radicals is partly via H/O ring substitution $\text{C}_7\text{H}_8 + \text{O} = \text{OC}_7\text{H}_7 + \text{H}$ (2). The rate has been adopted from Hoffmann et al. [7] who considered a temperature range of 1100 – 1350 K at a pressure of 300 Pa. Reaction (2) is interesting as it also initiates a primary C_6H_6 formation channel with OC_7H_7 eventually leading to benzene via fulvene. The calculated concentrations of $\text{C}_7\text{H}_6\text{O}$ are somewhat over-predicted and the primary channel at 1160 K is via thermal decomposition $\text{C}_7\text{H}_7\text{O} = \text{C}_7\text{H}_6\text{O} + \text{H}$ (3). The formation of $\text{C}_7\text{H}_7\text{O}$ is via O_2 and HO_2 attack on the benzyl radical and, in particular, the latter reaction is subject to significant uncertainties.

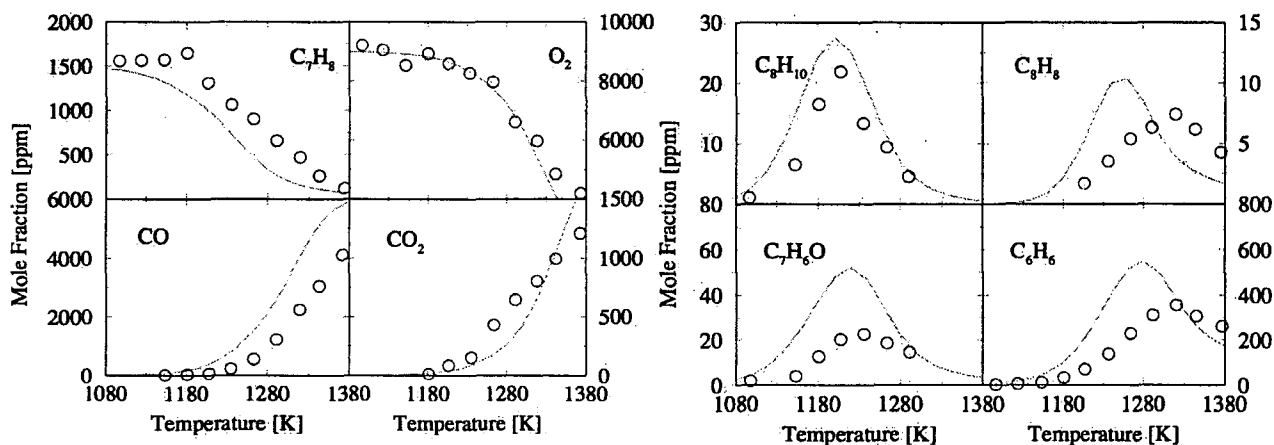


Fig. 1. Consumption of C_7H_8 and O_2 along with CO and CO_2 formation (left) and major primary intermediates (right) formed during the oxidation of toluene in a JSR [4].

The rate for reaction (3) was estimated from the heat of reaction (64 kJ/mol) plus an additional 4 kJ/mol and a frequency factor of $3.0 \times 10^{12} \text{ m}^3 \text{ kmol}^{-1} \text{ s}^{-1}$ was assigned. Alternative chemical mechanisms feature a rate expression with a high frequency factor ($1.3 \times 10^{14} \text{ m}^3 \text{ kmol}^{-1} \text{ s}^{-1}$) and a low barrier (4.6 kJ/mol), which is incompatible with the current data sets. The issue is raised as an illustration of current uncertainties. The developed toluene mechanism

does reproduce, with reasonable accuracy, the H radical concentrations formed during toluene pyrolysis, as measured by Braun-Unkoff et al. [8], and the more recent time resolved OH radical data obtained by Vasudevan et al. [9]. The corresponding 1-methyl naphthalene chemistry was derived directly from the toluene mechanism with appropriate adjustments (e.g. to frequency factors). The ability of the resulting mechanism to reproduce 1-methyl naphthalene JSR data was explored and the case presented here features $\phi = 1.5$, $1090 < T$ (K) < 1440 , a mean residence time of 100 ms and a pressure of 1 atm. Selected results are shown in Fig. 2 and principal reaction paths in Fig. 3. The overall agreement is encouraging with fuel and oxygen consumption along with levels of naphthalene and indene well reproduced. The small levels of (s,t)-C₉H₈ shown in Fig. 2 correspond to phenyl with C₃ side chains (ϕ -CHCCH₂ and ϕ -CH₂CCH) [10].

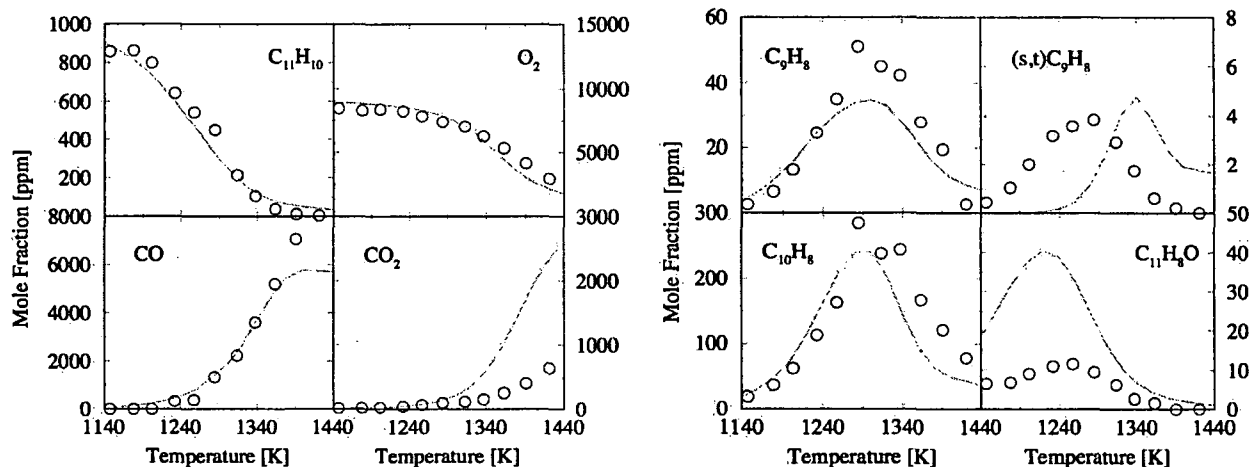


Fig. 2. Consumption of C₁₁H₁₀ and O₂ along with CO and CO₂ formation (left) and major primary intermediates (right) formed during the oxidation of 1-methyl naphthalene in a JSR at atmospheric pressure with a mean residence time of 100 ms [5].

The formation of C₁₁H₉ is predominantly via H (30%) and OH (15%) radical attack. The rate for the analogous C₇H₈ + OH step was used for the model reaction. The dominant channel for the corresponding abstraction to C₁₁H₉P is via OH radical attack and the rate for the analogous reaction was obtained from Baulch et al. [6]. The analogous [7] O atom attack on the ring also generates H radicals and consumes about 15% of the fuel at 1260 K. The subsequent formation of indene was based on an analogy with the C₆H₆/C₅H₆ system [11]. Similarly to the results obtained for toluene, the principal aldehyde (C₁₁H₈O) is overpredicted. The path responsible follows by analogy as C₁₁H₉O = C₁₁H₈O + H along with the uncertainties associated with O₂

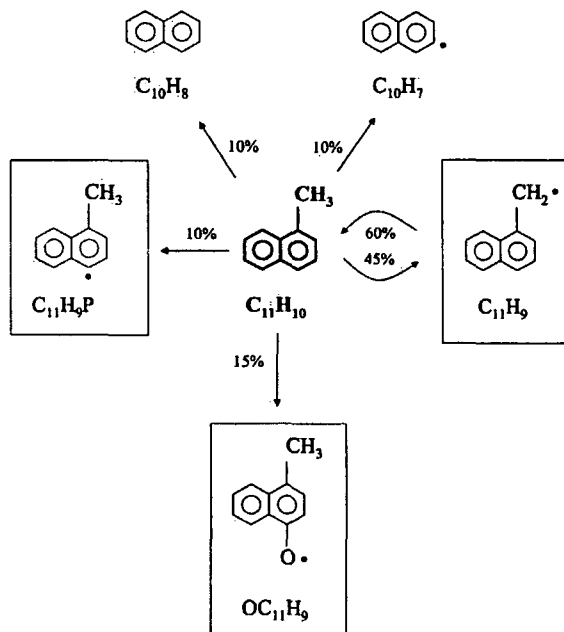


Fig. 3. Consumption paths of 1-methyl naphthalene in a JSR (T = 1260 K, P = 1 atm and $\phi = 1.5$).

and HO₂ attack on C₁₁H₉ as mentioned above in the context of the benzyl radical. The formation of naphthalene and the naphthyl radical follows via paths directly analogous with benzene formation from toluene. The extraction of CO from the C₆ ring, eventually leading to indene, follows from the work by Lindstedt and Rizos [11].

CONCLUSIONS

The current paper has sought to illustrate the use of a reaction class based approach for the oxidation of substituted aromatics. An analogy with toluene was used to develop a comprehensive detailed chemical kinetic mechanism for 1-methylnaphthalene with encouraging results. A particular benefit with the approach is that validation data from simpler systems can be used to mitigate the scarcity of such data for practical fuel components. The approach has also been used to create the basis of a simple two-component surrogate mechanism for Jet-A based on n-decane [12] and n-propyl benzene [13]. However, common problems were also found and, for example, predictions of C₇H₆O and C₁₁H₈O were found to be consistently high. Recent work on the toluene/benzyl system (e.g. [9]) opens up the possibility of removing such anomalies as part of the current grant. In future work, the mechanism generation part will be automated through the adaptation of an existing JAVA based tool developed for heterogeneous chemistry. It must also be emphasized that the creation of large detailed mechanisms is predominantly useful in the context of providing a reference frame for extrapolation to practical operating conditions and for further simplifications aimed at the inclusion of chemical kinetic effects into turbulent flows [14].

ACKNOWLEDGEMENT

The contributions made by M Potter are gratefully acknowledged along with the access to unpublished data obtained by P Dagaut and co-workers.

REFERENCES

- [1] Tishkoff, J.M., Drummond, J.P., Edwards, T. and Nejad, A.S., Paper AIAA 97-1017 (1997).
- [2] Lindstedt, R.P. and Maurice, L.Q., Combust. Sci. and Technol., 120:119-167 (1996).
- [3] Potter, M. L. Detailed Chemical Kinetic Modelling of Propulsion Fuels, PhD Thesis, Imperial College London, 2003.
- [4] Dagaut, P., Pengloan, G. and Ristori, A. Phys. Chem. Chem. Phys. 4: 1846 (2002)
- [5] Dagaut, P. Private Communication, March 2003.
- [6] Baulch, D.L. Cobos, C.J., Cox, R.A., Esser, C., Frank, P., Just, Th., Kerr, J.A., Pilling, M.J., Troe, J., Walker, R.W. and J. Warnatz, J., J. Phys. Chem. 21:411 (1992).
- [7] Hoffmann, A., Klatt, M. and Wagner, G. Gg., Z. Phys. Chem. 168:1 (1990)
- [8] Braun-Unkhoff, M., Frank, P. and Just, Th., Proc. Combust. Inst. 22:1053 (1988).
- [9] Vasudevan, V., Davidson, D. and Hanson, R.K. Proc. Combust. Inst 30:1155 (2005).
- [10] Lindstedt, R.P., Maurice, L.Q. and Meyer, M. The Royal Society of Chemistry, Faraday Discussion 119:409-432 (2001).
- [11] Lindstedt, R.P. and Rizos, K.-A., Proc. Comb. Inst. 29:2291-2298 (2002).
- [12] Lindstedt, R.P. and Maurice, L.Q. AIAA J. Propul. Power 16:187-195 (2000).
- [13] Final Report, Computational Fluid Dynamics for Combustion (CFD4C), CEC Project No: GRD1-1999-10325 (2003).
- [14] Kuan, T.S. and Lindstedt, R.P. Proc. Combust. Inst. 30:767 (2005).